PRODUCTION AND CHARACTERIZATION OF POLYMER BLEND FROM LDPE AND STARCH

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Thesis submitted in fulfillment of the requirements
for the award of the degree of
Bachelor of Chemical Engineering

Faculty of Chemical and Natural Resources Engineering
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JUNE 2012

ABSTRACT

Polymer blend is an alternative polymer to substitute a common polymer used in industrial. It acts same as the others polymer. The resource to make polymer blend is from the natural polymer. The combination of natural polymer and other polymer is called polymer blend. In this study, tapioca starch and low-density polyethylene (LDPE) had been used to form the polymer blend. A compatibilizer is required in order to allow starch and LDPE to get mixed. Citric acid is one of the most readily applicable agents Function of the compatibilizer is to fragment the bond of the combination polymer due to the acidity of citric acid is propitious and the ensuing dissolution of the tapioca starch granules. The objectives of this study are to improve production of polymer blend and optimum polymer composition. Formulation that had been set are from 5, 10, 15, 20 and 25% value of starch based on LDPE. The samples first undergo extrusion process that make the samples form into pellet size. Then, the pellet had been gone through molding process which is injection molding. The pellet been shaped into dumbbell shape for testing purpose. Characteristic that had been done are like tensile strength, density and water absorption. The result expected is to show the certain formulation gives high response in the area of testing and the optimum polymer blend composition is determined.

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CHAPTER 1

INTRODUCTION

1.1 Research Background

Polymer blend from renewable resources have attracted all attention over the last twenty five years because of due to two major factors: firstly environmental issues, and secondly the realization that the petroleum resources are finite (Yu *et al*., 2006). The polymer blend is alternative materials that have been produced with desirable properties based on available polymers rather than to design and synthesize a new polymer. For these reasons, the demands for polymer blend are really high in the market.

Polymer blend have attributed many functions to industrials sector and gain popularity through it. Many goods are made from polymer blends and it is usually cheaper and less time-consuming (He *et al*., 2004). The application of polymer blend is use in numerous sectors such as; adhesion, colloidal stability, and design of composite and biocompatible materials (Lipatov, 2002). Basically, polymer blend are produced by combining polymers and changing the blend composition of product that have been use.

Material that normally been used to produced polymer blend is belong to polysaccharides group which are cellulose, pectin, gums, caragreenan and starch. From all the materials, starch is a potential material since its inherent biodegradability, overwhelming abundance and its annual renewal compare to the others. However, the pure starch needs to add plasticizer due to solve water soluble, difficult to process and brittle problems (Yu *et al*., 2006).

The common method to convert raw starch into polymer blend is by using reactive extrusion. The reactive extrusion is take place in batch or continuous stirred tank reactors. The reactive extrusion process can be simply described as gelatinization then results in disruption follow by formation and end with modification process. The material which is starch undergoes gelatinization in hot water for certain temperature resulting in disruption of starch granule and formation of homogenous solution based on the starch. Finally, the substance goes through modification process at relatively low reaction temperature and with high salt and water concentrations. For this process, temperature and composition of water and starch influence the process which causes the poor and good reaction selectivity (Moad, 2010).

1.2 Identification of Problem

Polymer blend is an alternative polymer to substitute a common polymer used in industrial. It acts same as the others polymer. The advantage using the polymer blend is because it is inherently biodegradable. Currently, whole world-wide have concern how important the environmental issues. By using the polymer blend, means that it can control the environment furthermore can create new applications from it (Yu *et al.*, 2006).

The low costing for making the polymer blend have make it more preferable to be used. They represent one of the most rapidly factors in polymer science material. However, the polymer blend also have it disadvantages are their dominant hydrophilic character, fast degradation rate and unsatisfied mechanical properties (Yu *et al.*, 2006). But compare to the synthetic polymer which are not degradable, have environmental problem and limited resources, clearly the needed for other alternative is high. Based on that statement, a proposal on a new production and characterization of polymer blend by knowing the addictives that been used to improve their process ability and properties in term of mechanical strength to determine the best polymer compositions have been clarified.

1.3 Statement of Objectives

The main objectives of this study to improve the production of polymer blend via injection molding, to perform characterization of polymer blend and to determine the optimum polymer composition via mechanical testing.

1.4 Research Scopes

The research scopes for this study are:

i. To improve the productions of polymer blends at fix composition of plasticizer and different composition of LDPE and starch.
ii. To perform the characterization of polymer blends in terms of mechanical properties of the polymer blends such as tensile strength, and elongation.
iii. To determine optimum polymer blend production based on the composition of LDPE and starch, where measure in terms of mechanical properties.

1.5 Rationale and Significance of Study

Polymer blend basically a combination of two or more polymers produce by blends them together to make a new product with unique properties. A study shown over 30% of polymers that have been used world-wide are from polymer blends (Alam *et al.*, 2005) and it suggest that the demand for polymer blends is currently rising. From this perspective, the polymer blend is a promising alternative because of several advantages; it is renewable, biodegradable, and less-consuming. The production of polymer blend from starch are really suitable to be make as Malaysia have many sources of starch such as tapioca, potato and corn. The polymer blend that will be produce should have different properties although the products for blending have different properties.

The costing for production of polymer blend is lower compares to production of new polymer. Therefore, the demands of polymer blend in plastic sector rising because of its properties. It also proved that polymer blending is one of simple and efficient in developing high performance of composite system (Pinchuk *et al.*, 2003). For this purpose, the production of polymer blend can be use world-wide especially in Malaysia since the source of natural polymer like starch can be obtains. By commercially using polymer blend, it also can save the environment since it is a biodegradable product.

CHAPTER 2

LITERATURE REVIEW

2.1 Overview of Polymer Blend

For the development of new polymeric materials, polymer blending is a convenient route for this goal and it produce polymer blend. Compare to the individual components properties, the process able to yield materials with properties profiles superior than the components. In addition, this process is usually cheaper and less time-consuming for the production of polymer materials with new properties than the development of new monomers or new polymerization routes. Polymer blend's advantage is that the properties of the materials can be altered by combining component polymers and changing the blend composition (He *et al.*, 2004).

There are three different types of polymer blend can be categorized: firstly is completely miscible blends, secondly partially miscible blends and lastly fully immiscible blends. Miscible can be defined as where the two or more liquid can be mixed together. Besides that, polymer blends are either exists in homogeneous or heterogeneous state. In homogeneous blends, the average properties of the blend components are the final properties which means the properties is divided equally. Meanwhile in heterogeneous blends, the properties of all blend components are present (Yu *et al.*, 2006 & He *et al.*, 2004).

2.2 Polymer Blend Production

The process to produce polymer blend is by polymer blending. This method is combination of two or more polymer by blending it together. The properties obtain from new material usually have different properties from the original properties. Normally the polymer blend use sources like natural polymer. This is because the natural polymer is easy to get, totally biodegradable and inexpensive. Examples of natural starch have been shown in Figure 2.1. For this study, starch has show potential as the natural polymer due to its ability and desirable properties.

Table 2.1: List of natural polymer (Yu *et al.*, 2006)

Natural polymer
Polysaccharides • Plant/algal: cellulose, pectin, konjac, alginate, starch, caragreenan, gums • Animal: hyluronic acid • Fungal: pulluan, elsinan, scleroglucan • Bacterial: chitin, chitosan, levan, xanthan, polygalactosamine, curdlan, gellan, dextran
Proteins Soy, zein, wheat gluten, casein, serum, albumin, collagen/gelatin, silks, resilin, polylysine, polyamino acids, poly(γ-glutamic acid), elastin, polyarginyl-polyaspartic acid
Lipids/surfactants Acetoglycerides, waxes, surfactants, emulsan
Speciality polymers Lignin, shellac, natural rubber

One of the main disadvantages of biodegradable polymers obtained from renewable sources is their dominant hydrophilic character, fast degradation rate and, in some cases, unsatisfactory mechanical properties, particularly under wet environments. In principle, the properties of natural polymers can be significantly improved by blending with synthetic polymers for example is polyethylene.

Polymer blending is a well-used technique whenever modification of properties is required, because it uses conventional technology at low cost. However, in the production of polymer blend there are several problem might occurs; water

soluble, difficult to process and brittle. Therefore to solve the problems is to add plasticizer to the blend (Yu *et al.*, 2006). By embedding themselves between the chains of polymers, and spacing them apart is how the plasticizer works.

2.2.1 Melt Processed Blends

Starch is one of the most promising natural polymers because of its inherent biodegradability, overwhelming abundance and its annual renewal. However, by itself, pure starch is not a good choice to replace petrochemical-based plastics. It is mostly water soluble, difficult to process and brittle when used without the addition of a plasticizer. In addition, its mechanical properties are very sensitive to moisture content. Blending two or more chemically and physically dissimilar natural polymers has shown potential to overcome these difficulties.

2.2.2 Aqueous Blends

Many natural polymers cannot be melt processed, either because they degrade on or before melting (softening) or because they are designed to incorporate substances that do not stand high temperature (proteins, drugs, etc.). For these examples, aqueous blending is the preferred technology, particularly in biomedical applications.

Natural polymers are usually biocompatible and non-cytotoxic due to their similarity with living tissues. Biopolymers are an important source of material with a high chemical versatility and with high potential to be used in a range of biomedical applications. A great variety of materials derived from natural sources have been studied and proposed for different biomedical uses, namely polysaccharides (starch, alginate, chitin/chitosan) or protein (soy, collagen, fibrin gel) and, as reinforcement, a variety of biofibers such as lignocellulosic natural fibers. Starch-based polymers present enormous potential for wide used in the

biomedical field, as these natural polymers are totally biodegradable and inexpensive when compared to other biodegradable polymers available. Aqueous blends of soluble starch and cellulose acetate have been studied intensively because these blends have a range of properties that make them suitable for use in a wide array of biomedical applications, ranging from bone replacement to engineering of tissue scaffolds and drug-delivery systems.

2.3 Starch

Starch is a polysaccharide carbohydrate and a complex carbohydrate. The chemical formula for starch is $(C_6H_{10}O_5)_n$. It is consisting of amylose (linear chain of glucose) and amylopectic (branched chain of glucose). Starch is a polysaccharide produced by mostly higher order plants as a means of storing energy. Most commercially available starches are isolated from grains such as corn, rice and wheat, and from tubers such as potato and tapioca (Liu *et al.*, 2009 & Dona *et al.*, 2010).

Tapioca starch is very cheap and readily available in Malaysia which has made this product chosen among different kinds of starch. Starch also as an old source of food for human and animals has been known for centuries (Abolhasani *et al.*, 2010). Composition of the tapioca root is moisture (70%), starch (24%), fiber (2%), protein (1%) and other substances including minerals (3%). The starch composition in tapioca is quite higher compare to the other sources (Liu *et al.*, 2009).

Tapioca starch has been used world-wide and the in industrial application such as textiles, paper, detergent soap, and as well used as adhesive and glue (Matzinos *et al.*, 2002). Since the tapioca starch has been used and many usage can be gain from it, the tapioca starch have exploited and been used to produce polymer based products.

2.3.1 Starch Composition and Structure of Component

Starch is a polymeric carbohydrate consisting of anhydroglucose units linked together primarily through α-d-(1→4) glucosidic bonds. Although the detailed microstructures of different starches are still being elucidated, it has generally been established that starch is a heterogeneous material containing two microstructures linear is amylose and branched is amylopectin (Le *et al.*, 2009 & Liu *et al.*, 2009).

Amylose is essentially a linear structure of α-1,4 linked glucose units, and amylopectin is a highly branched structure of short α-1,4 chains linked by α-1,6 bonds. Figure 2.1 shows the chemical structure and a schematic representation of amylose and amylopectin starches. The linear structure of amylose makes its behavior more closely resemble that of conventional synthetic polymers (Tester *et al.*, 2003, Moad, 2011 & Liu *et al.*, 2009).

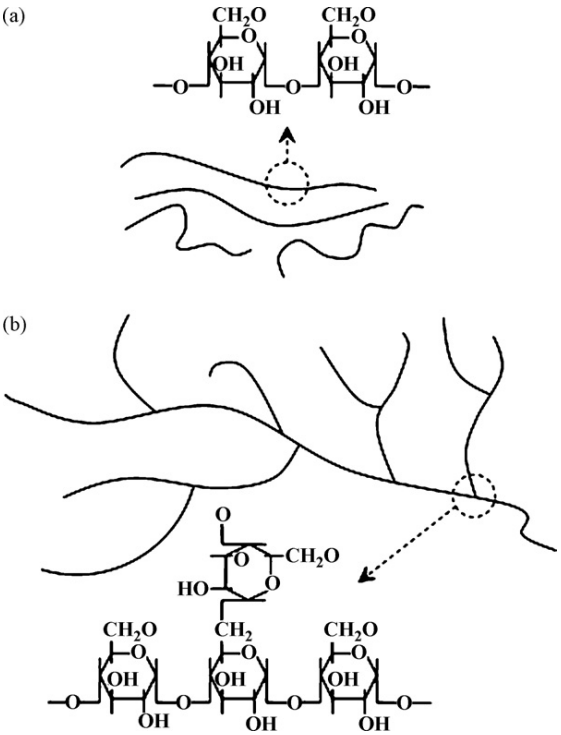

Figure 2.1: Chemical structures and physical schematic representation of (a) amylose starch and (b) amylopectin starch. (Liu *et al.*, 2009)

Amylopectin, on the other hand, is a branched polymer and its molecular weight is much greater than amylose, with light-scattering measurements indicating molecular weights in the millions. The high molecular weight and branched structure of amylopectin reduce the mobility of the polymer chains, and interfere with any tendency for them to become oriented closely enough to permit significant levels of hydrogen bonding. Between the linear amylose and short-branched amylopectin, a long-branched structure has been detected and it can be seen in tapioca starch (Tester *et al.*, 2003, Moad, 2011 & Liu *et al.*, 2009).

2.4 Polyethylene (PE)

Polyethylene is a type of polymer that is classified as a thermoplastic, meaning that it can be melted to a liquid and remolded as it returns to a solid state. As the name implies, polyethylene is chemically synthesized from molecules that contain long chains of ethylene, a monomer that provides the ability to double bond with other carbon-based monomers to form polymers. Polyethylene is known by other, non-official names, such as polythene in the United Kingdom. In addition, it is sometimes spelled as polyethylyne, or abbreviated to simply PE.

The first laboratory creation of polyethylene occurred in 1898 by accident at the hands of Hans von Pechmann while applying heat to another compound the German chemist previously discovered; diazomethane. Ironically, the synthesis of polyethylene via extreme heat and pressure in an industrial setting was again made by accident, but 35 years later. A few years later, another chemist employed by the same England-based chemical company devised a method to consistently produce polyethylene under the same conditions. As a result, polyethylene became the primary source of low-density polyethylene (LDPE) production in 1939 (Sailaja & Seetharamu, 2007).

2.4.1 Low Density Polyethylene (LDPE)

Low density polyethylene (LDPE) is one of thermoplastic type plastic. Generally, it produces from petroleum at high temperature process. LDPE exists in solid particle form, with a density of 0.93 g/cm3 and a melt index of 2.5 g/min. LDPE contains the saturated C–C and C–H bonds, and shows the properties of nonpolarity, low surface energy and poor hydrophilic (Yang *et al.*, 2008). LDPE is from synthetic polymer group and plays important roles in polymer blend production as compatibilizer (Sailaja & Seetharamu, 2007).

2.4.2 High Density Polyethylene (HDPE)

HDPE is the high density version of PE plastic. It is harder, stronger and a little heavier than LDPE, but less ductile. HDPE is lighter than water, and can be molded, machined, and joined together using welding (difficult to glue). The appearance is wax-like, lustreless and opaque. The use of UV-stabilizators (carbon black) improves its weather resistance but turns it black. Some types can be used in contact with food (Yang *et al.*, 2008).

2.5 LDPE and Starch Combination

Through blending process, LDPE and starch could be mix together to form a new polymer blend. However, LDPE and starch itself cannot mix easily due to water soluble matter. Therefore, plasticizers and addictives such as glycerol, citric acid and stearic acid can be used to solve the matters (Liu *et al.*, 2009 & Chillo *et al.*, 2008). The addictives and compatibilizer help the molecule to attach to each others. To produce this process starch based material, such as extrusion, injection molding and film casting, are similar to those widely used in the processing of traditional petroleum based material. The processing of starch, however, is much more complicated and different to control. This is because the unsatisfactory processing

properties as a result of its unique phase transitions, high viscosity, water evaporation and fast retrogradation (Liu *et al.*, 2009). To solve this problem, proper formulation development and suitable processing conditions need to be done. The formulation development include: adding appropriate plasticizers, adding appropriate lubricants, using modified starch and using copolymers of starch graft hydrophobic polymer (Matzinoz *et al.*, 2002).

2.6 Effect of Addictives and Plasticizer

A starch-based polymer cannot be thermally processed without a plasticizer or gelatinization agent, since its decomposition temperature is lower than its melting temperature before gelatinization. Various plasticizers and additives have been evaluated and developed to gelatinize starch during thermal processing. Water is the most popular plasticizer used in the thermal processing of starch-based polymers, indeed cooking starches with water has been practiced for hundreds of years. Various other plasticizers to improve the processing properties and product performance of thermoplastic starch have been evaluated, and various polyols have been widely used, e.g. glycerol glycol and sorbitol (Liu *et al.*, 2009). LDPE was utilized as the backbone in binder formulation. A compatibilizer is required in order to allow the thermoplastic and LDPE to get mixed. Citric acid is one of the most readily applicable agents (Abolhasani *et al.*, 2010).

2.6.1 Glycerol

The function of glycerol attend in the thermoplastic starch are because it can result in a reduction in apparent viscosity. In addition, a reduction in *K* has been attributed to the plasticizing effect of glycerol (Sailaja & Seetharamu, 2007 & Liu *et al.*, 2009).

2.6.2 Citric Acid

To mix between starch and LDPE, the citric acid must be used. This is because the acidity of citric acid is propitious to fragmentation and the ensuing dissolution of the tapioca starch granules deteriorates the chain entanglements in the starch and weakens the interactions between the starch molecules, which in turn facilitates the slipping movement among starch molecule (Liu *et al.*, 2009).

2.6.3 Stearic Acid

It also necessary for stearic to be add to polymer blend production from LDPE and starch. The stearic acid acts as a surfactant agent to bridge between binder and metal powder. It has shown that the stiffness of the binder at room temperature was reasonably acceptable that would ensure the polymer blend strength (Abolhasani *et al.*, 2010).

CHAPTER 3

RESEARCH METHODOLOGY

3.1 Material and Solvent

Citric acid was procured from Sigma-Aldrich will be used as additives for polymer production. Glycerol solution will be used as plasticizer in the blending solution. In extrusion reaction, the feedstock are LDPE pellet and starch powder are been used. Water also will be used in blending process for thermal purposes.

3.2 Apparatus

The apparatus that will be used in this experiment are extruder and hot press machine. Detail explanations are provided in Section 3.2.1, and 3.2.2.

3.2.1 Extruder

Extruder as illustrated in Figure 3.1 is the equipment that will be used in this research for blending process. The extruder is for the extrusion process. It designed to produce long continuous products such as tubing, wire covering, and tire threads. The extruder generally consists of the material feed hopper, basic extruder, the extrusion die, the calibration units, the haul-off, cutting device, and finally the devices for treatment final finishing and handling. The basic extruder type usually use is screws, however in some extruder the type is different such as drive or gearbox.

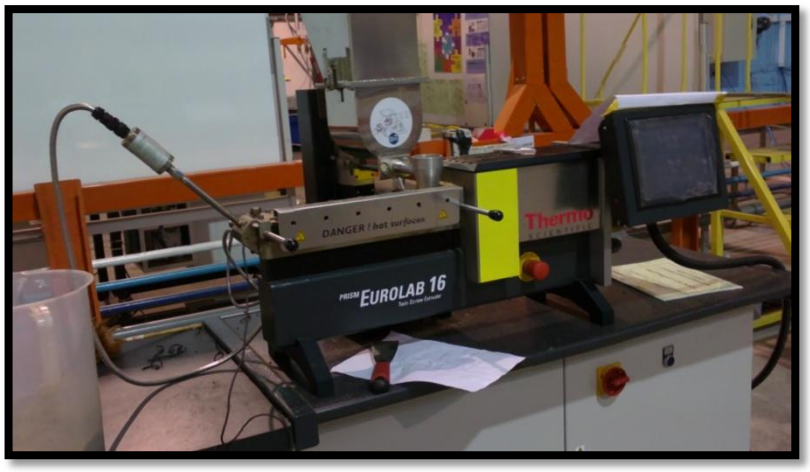

Figure 3.1: Extruder machine

3.2.2 Hot Press Machine

Hot press machine is a machine use to forming object according to mold that been used by using press method. The machine use pressure that will press the two plate which are in high temperature. Thus to forming a dumbbell shape for testing analysis can be achieve by heat and pressure supply by the machine. The heat will melt the polymer so that it can form shape according to the mold. The hot press machine is illustrated in Figure 3.2.

Figure 3.2: Hot press machine

3.3 Experimental Work

3.3.1 Sample Preparation

Based on Table 3.1, the material are been weight according to the right weight. It is 5 sample after all the material been weight and been mixed. The sample had been categorized based on starch weight percentages.

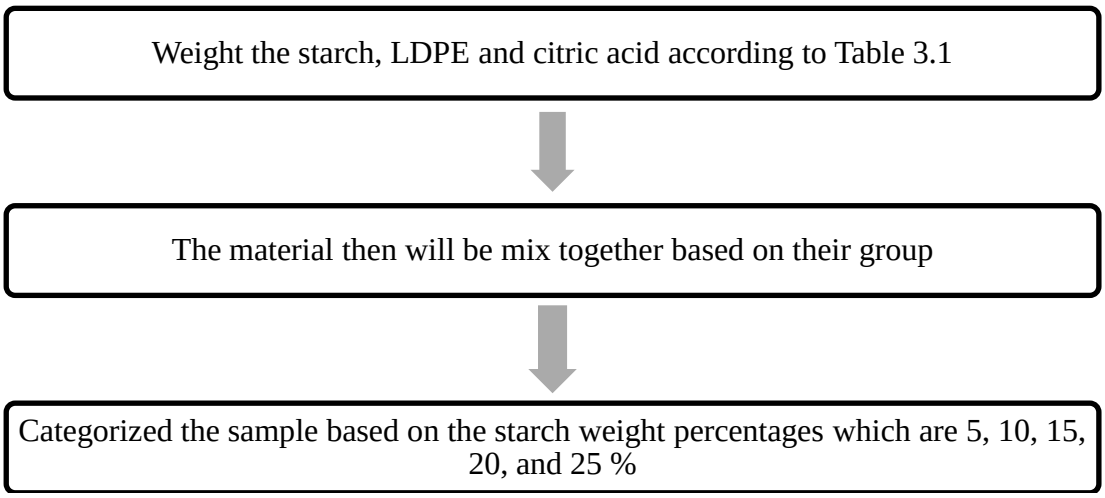

Figure 3.3: The flow chart for sample preparation

Table 3.1: Ratio of LDPE, starch and citric acid that want to be study

LDPE Basic Weight (g)	Starch (wt%)	Citric acid (wt%)
300	5	3
300	10	3
300	15	3
300	20	3
300	25	3

3.3.2 Extrusion Process

In this work, a blend of starch, distilled water, citric acid and glycerol will be mix, and then be heat in the extruder machine to make a yellow transparent fluid, which could be considered as thermoplastic starch. At the extruder machine, six value of temperature should be set which are for zone 2, zone 3, zone 4, zone 5, zone 6 and die. All the temperatures are different starting from zone 2 until die sections which are 140, 145, 150, 155, 145 and 140°C. The excess water content in the mixing will be evaporates due to the working point temperature. The temperatures that had been set will ensure combination of LDPE and starch to melt. The screw rotation speed for extruder will be set about 70 rpm. Lastly, the continuous pallet will be form.